THEORETICAL STUDIES ON THE THERMAL DEGRADATION OF LADDER POLYMERS

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FOREWORD

This report was prepared by the Polymer Branch of the Nonmetallic Materials Division. The work was initiated under Project No. 7342, "Fundamental Research on Macromolecular Materials and Lubrication Phenomena," Task No. 734203, "Fundamental Principles Determining the Behavior of Macromolecules." It was administered under the direction of the AF Materials Laboratory, Research and Technology Division, Lt. Martin M. Tessler, project engineer.

This report covers work accomplished January 1963 to December 1963.

ABSTRACT

The random thermal degradation of four- and six-membered ring ladder polymers were investigated and results compared to a single chain polymer undergoing degradation under the identical conditions. The change in molecular weight versus time was plotted and significant differences were found in the shapes of the curves.

Similar studies were conducted with imperfect ladder polymers which had single bonds along the backbone of the polymer.

This technical documentary report has been reviewed and is approved.

William E. Gibbs

WILLIAM E. GIBBS
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TABLE OF CONTENTS

ILLUSTRATIONS

ILLUSTRATIONS (CONT'D)

INTRODUCTION

Interest in the development of thermally stable materials has produced much research into new and novel types of polymers. One area of investigation is the preparation of a ladder or double-strand polymer. The first successful synthesis of a ladder polymer was reported by Brown and co-workers (Reference 1). They prepared the double-chain polyphenylsilesquioxane in which the polymer backbone is completely inorganic. Attempts to synthesize a ladder polymer with an organic backbone from vinyl isocyanate (Reference 2) poly-3,4-isoprene (Reference 3) and conjugated dienes (Reference 4) have recently been reported. These polymers have segments of fused rings, but they are not completely fused into the desired ladder structure.

This report compares the thermal stability of a ladder polymer undergoing random degradation with that of a single chain polymer. A digital computer is used to set up a statistical (Monte Carlo) (Reference 5) model of the degrading system. The following assumptions are made in defining the degrading system:

1. The polymer sample is initially homogeneous; that is, only chains of one length are present.

2. All bonds in the polymer chain are of equal strength and equal accessibility, regardless of their positions in the molecule and the length of the chain.

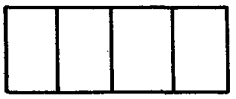
3. The rate of breaking of bonds is proportional to the number of bonds present in the degrading system.

4. The system is closed; that is, no fragments can leave the system.

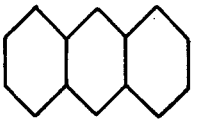
The ratio of the number average molecular weight (at time kt) to the initial number average molecular weight is obtained directly from the computer, where k is the proportionality constant between the rate of breaking bonds and the number of bonds present in the system at time t.

MODEL LADDER STRUCTURES

Two types of ladder polymers were studied. Type I is a fused four-membered ring and Type II is a fused six-membered ring. All the conclusions reached for a four-membered ring are equally applicable to an eight-membered ring.



TYPE I



TYPE II

Manuscript released by the author April 1964 for publication as an RTD Technical Documentary Report.

Initially, a simplified scheme of degradation was considered. In this simple case, a broken bond can break a molecule only if the bond opposite it is broken. The fact that a broken crosslink will increase the probability of a molecule breaking is ignored. This type of degradation is shown in Figure 1. The complex case of degradation is shown in Figure 2 where breaks in the crosslinks will result in increased molecule breaks. This is a much more realistic picture of random degradation than the simple case.

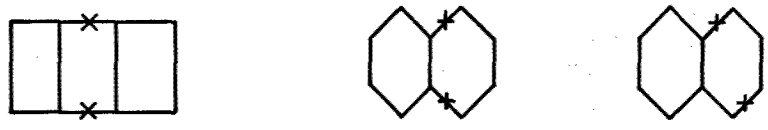
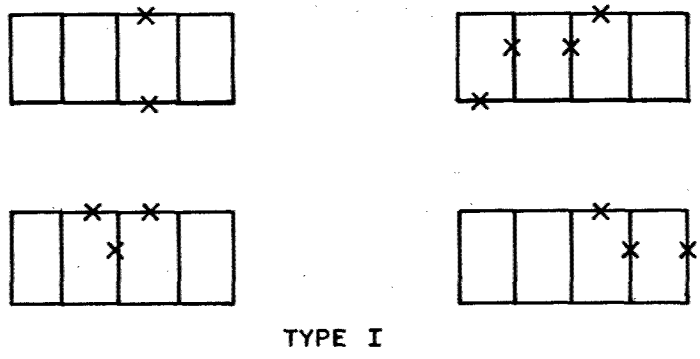


Figure 1. Different Ways a Molecule Can Break - Simple Case



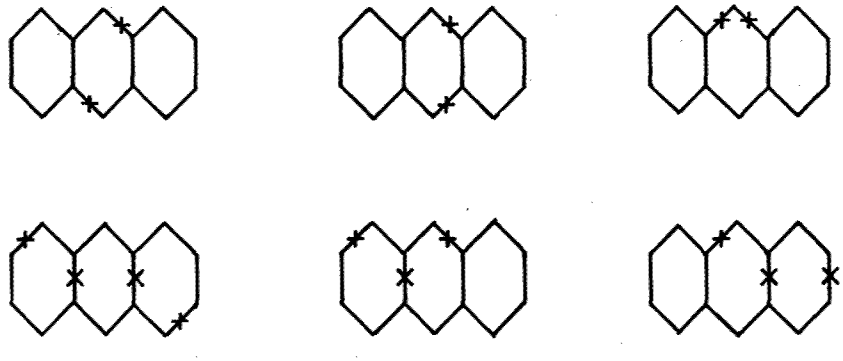


Figure 2. Different Ways a Molecule Can Break - Complex Case

MONTE CARLO MODEL

To construct a Monte Carlo model for the degradation reaction, a portion of the computer storage is set aside to represent the polymer molecules. Each storage location represents one bond. If a bond is broken, the number one is stored in its location and if it is not broken, a zero is stored there. Initially, all the storage locations are set to zero.

A random number is generated which has the limits of O and B_O-1, where B_O is the total number of bonds initially present in the system. Each number then represents a particular bond in a particular molecule and the number of molecules and the number of bonds per molecule can be varied at will with the limiting factor being the size of the computer storage. In the present study, a system of 100 molecules with 199 bonds per molecule for ladder polymer Type I and 100 molecules with 196 bonds per molecule for ladder polymer Type II were chosen. Simultaneously, a single chain polymer with the same number of bonds per molecule was degraded in the computer for comparison purposes.

When a random number is generated, the bond which it represents is checked to see if it is broken or not. If it is already broken, a duplicate is recorded and a new random number generated. If it is not broken, the bond is set equal to one and the opposite bond checked. If the opposite bond is broken, a broken molecule is recorded and a new random number is then generated. If the opposite bond is not broken, no further work is done in the simple case and a new random number is generated. In the complex case, the computer checks all the crosslinks to the left and right until it either comes to an unbroken crosslink or the last crosslink at the end of the molecule. If the last crosslink is broken, a broken molecule is recorded and a new random number generated. If the computer finds an unbroken crosslink, it then scans all of the side chain bonds on both sides of the ladder polymer from the broken bond produced by the random number generation to the last side chain bond before the unbroken crosslink. If any of the side chain bonds are broken, a broken molecule is recorded and a new random number is then generated. If none of the side chain bonds are broken, a new random number is generated. The computer keeps track at all times of the number of duplicates recorded. The number of bonds which are broken is equal to the number of random numbers generated minus the number of duplicates.

The number of molecules present in the system (at time kt) is equal to the number of molecules initially present plus the number of broken molecules since each broken molecule produces one more fragment. The time factor (kt) is equal to $\ln (B_O/B)$ where B_O is the number of bonds present initially and B is the number of bonds present at time kt. The ratio of the number average molecular weight at time kt, to the initial number average molecular weight is equal to 100/(100 + number broken molecules). All of these quantities are readily calculated during the course of the degradation and the computer prints out the desired data at any convenient interval of kt.

The subprogram by which the computer generates a random number makes use of an equation in which multiplication and division are used, the output being the remainder after division. Several different sets of random numbers were used to check the accuracy of the method. The random number generator appears to be very accurate and reliable.

RESULTS FOR PERFECT LADDER POLYMERS

The curve for the ratio of the number average molecular weight at time kt to the initial number average molecular weight versus kt is shown for ladder polymer Type I in Figure 3 and for ladder polymer Type II in Figure 4. Both the simple case and the complex case are shown as well as the analogous single chain polymer. The proportionality constant k is not known and it probably will have different values for different polymers.

This will shift the curves, but the significant fact is the shapes of the curves. The single chain polymer shows a very sharp drop in molecular weight as soon as degradation begins. The ladder polymer has an induction period where the molecular weight hardly changes and then it drops much more slowly than the corresponding single chain polymer. As degradation proceeds, both curves merge together. These results indicate that the ladder polymers should have increased thermal stability over single chain polymers, but the extent of this stability can only be determined by studying the chemistry of these compounds.

IMPERFECT LADDER POLYMERS

Ladder polymers are of interest because of their potential stability at high temperatures. The double-chain polyphenylsilsesquioxane, synthesized by Brown and co-workers (Reference 1) has an inorganic ladder structure and the silicon-oxygen bonds rearrange at elevated temperatures. The reported attempts to synthesize ladder polymers with an organic ladder structure (References 2, 3 and 4) have all used the same general approach. A polymer is first prepared which has pendant nonconjugated 1,6 unsaturation along the chain of the molecule. Overberger and co-workers (Reference 2) polymerized vinyl isocyanate through the vinyl group or the isocyanate group to get the starting polymer. Angelo (Reference 3) prepared poly-3,4-isoprene and Gaylord and co-workers (Reference 4) used butadiene, isoprene and chloroprene to obtain the desired polymer. Cyclization of the pendant nonconjugated 1,6 unsaturated polymer with suitable catalysts produces a ladder structure.

The problems in preparing a completely perfect ladder polymer are enormous. Imperfect ladder polymers can result from isolated unreactive groups, from alternative cyclizations or isomerizations, from crosslinking and from chain scission reactions. Extremely dilute solutions must be used to prevent crosslinking. Another problem is that as the ladder polymer is being synthesized, it solubility is decreasing rapidly and it may precipitate out of solution before ring closure is complete. If the polymer with the pendant nonconjugated 1,6 unsaturation is not structurally perfect, complications will arise in the cyclization step. For example, the poly-3,4-isoprene used by Angelo contained up to 10 percent of 1,4 structural units.

The difficulty in preparing perfect double-chain polymers raises the question as to how the thermal stability of an imperfect ladder polymer compares with that of a single chain polymer. A partial solution to this problem can be obtained by setting up in the storage of a digital computer, an imperfect ladder polymer. Each storage location will correspond to a different bond and a random number generator will be used to locate the bond which is being broken during degradation. An unbroken bond will be represented by a zero and a broken bond by a one. If all the bonds are initially set equal to zero, we will have a perfect ladder polymer. If we initially set a bond equal to one at prescribed intervals along the chain we will have an imperfect ladder polymer with the "broken bonds" corresponding to missing bonds in an imperfectly synthesized ladder polymer. If the random number generator should produce a number corresponding to one of these missing bonds, a duplicate will be recorded and a new random number will be generated without any further calculations. It is assumed that the polymer sample is homogeneous, all bonds in the polymer have an equal probability of being broken, the rate of breaking bonds is proportional to the number of bonds present in the degrading system and no fragments can leave the system.

The Monte Carlo calculations are identical to those described previously.

Four- (Type I) and six- (Type II) membered ring ladder polymers were studied and both the simple and complex cases of degradation examined. A single chain polymer with the same number of bonds per molecule was degraded simultaneously in the computer for comparison purposes.

Type I ladder polymers were studied with single bonds first at every sixth and then at every twelfth bond along the chain. Type II ladder polymers were studied with single bonds first at every twelfth and then at every twenty-fourth bond along the chain.

RESULTS FOR IMPERFECT LADDER POLYMERS

The introduction of single bonds along the chain of the ladder polymer results in a sharp decrease in molecular weight, as degradation occurs, compared to a perfect ladder polymer. The stability of the imperfect ladder polymer is still much greater than that of an analogous single chained polymer. The shape of the curves when the ratio of the number average molecular weight at time kt to the initial number average molecular weight is plotted against kt is very interesting. With a small number of single bonds within the ladder chain, the curves still have an induction period where the change of molecular weight is relatively small. It then drops very rapidly, although not as fast as a single chain polymer. As the number of single bonds are increased, the induction period disappears and the shape of the curve is the same as that of the single chain polymer although the molecular weight still does not decrease as fast. With a suitable value of k, it is possible that the curves will become superimposable and that the imperfect ladder polymer will have no increased advantage in thermal stability over a single chain polymer. The answer to this problem must await the synthesis and characterization of imperfect ladder polymers and a study of their chemical behavior when undergoing thermal degradation.

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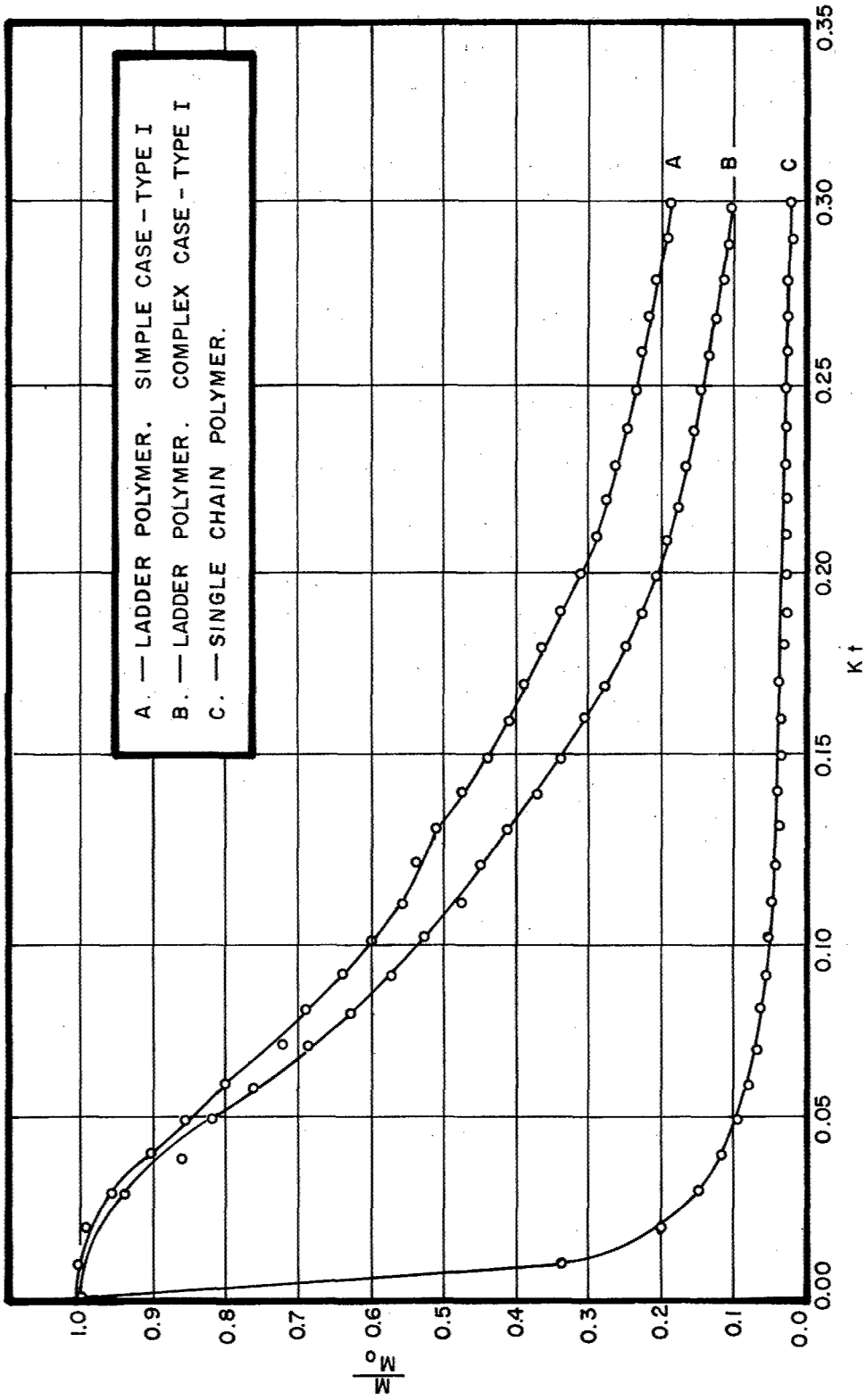

Figure 3. Plot of the Ratio of Molecular Weight to Initial Molecular Weight Versus Time for Different Polymers Undergoing Random Thermal Degradation

A. Ladder Polymer. Simple Case - Type I
B. Ladder Polymer. Complex Case - Type I
C. Single Chain Polymer

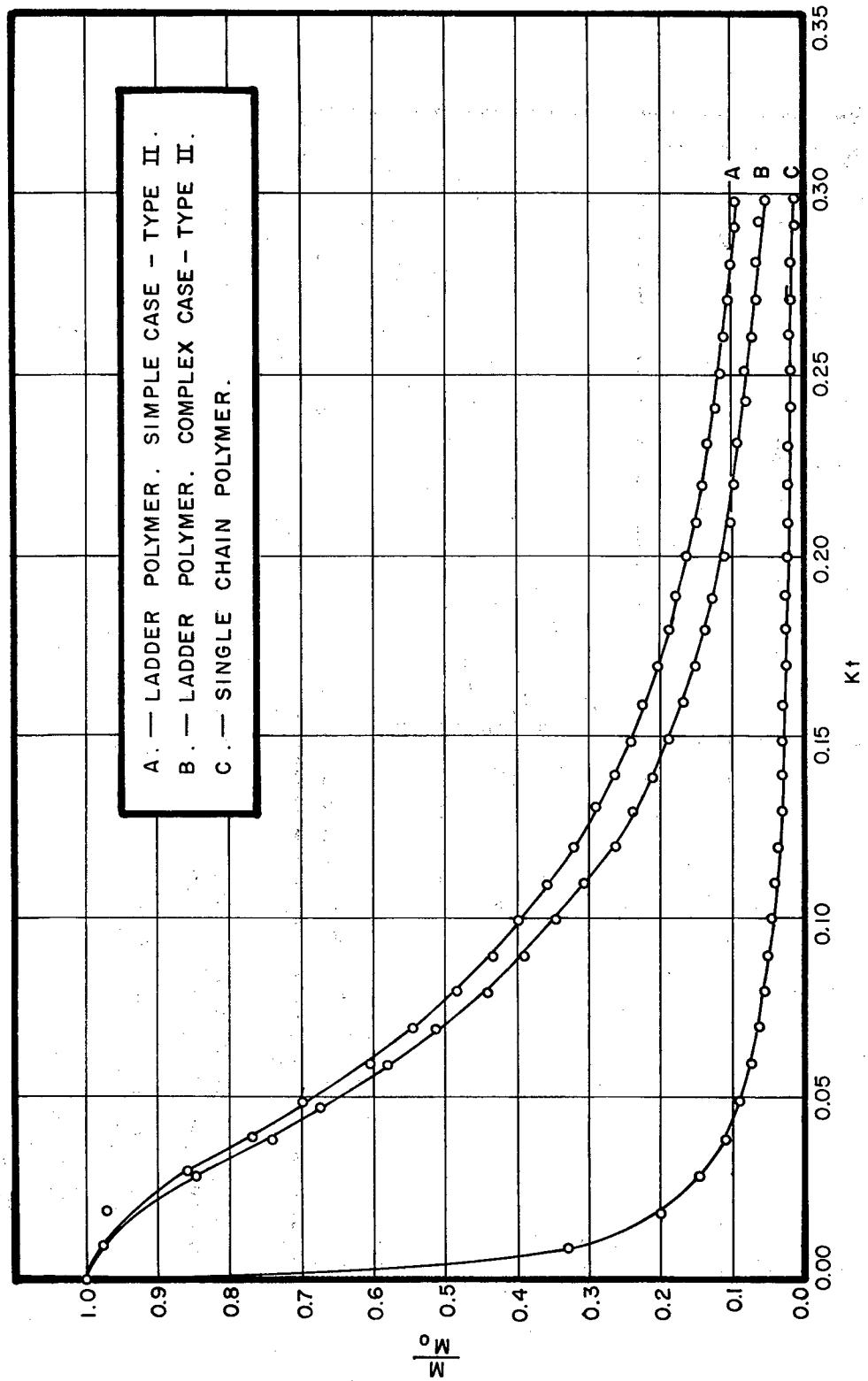

Figure 4. Plot of the Ratio of Molecular Weight to Initial Molecular Weight Versus Time for Different Polymers Undergoing Random Thermal Degradation

A. Ladder Polymer. Simple Case - Type II
B. Ladder Polymer. Complex Case - Type II
C. Single Chain Polymer

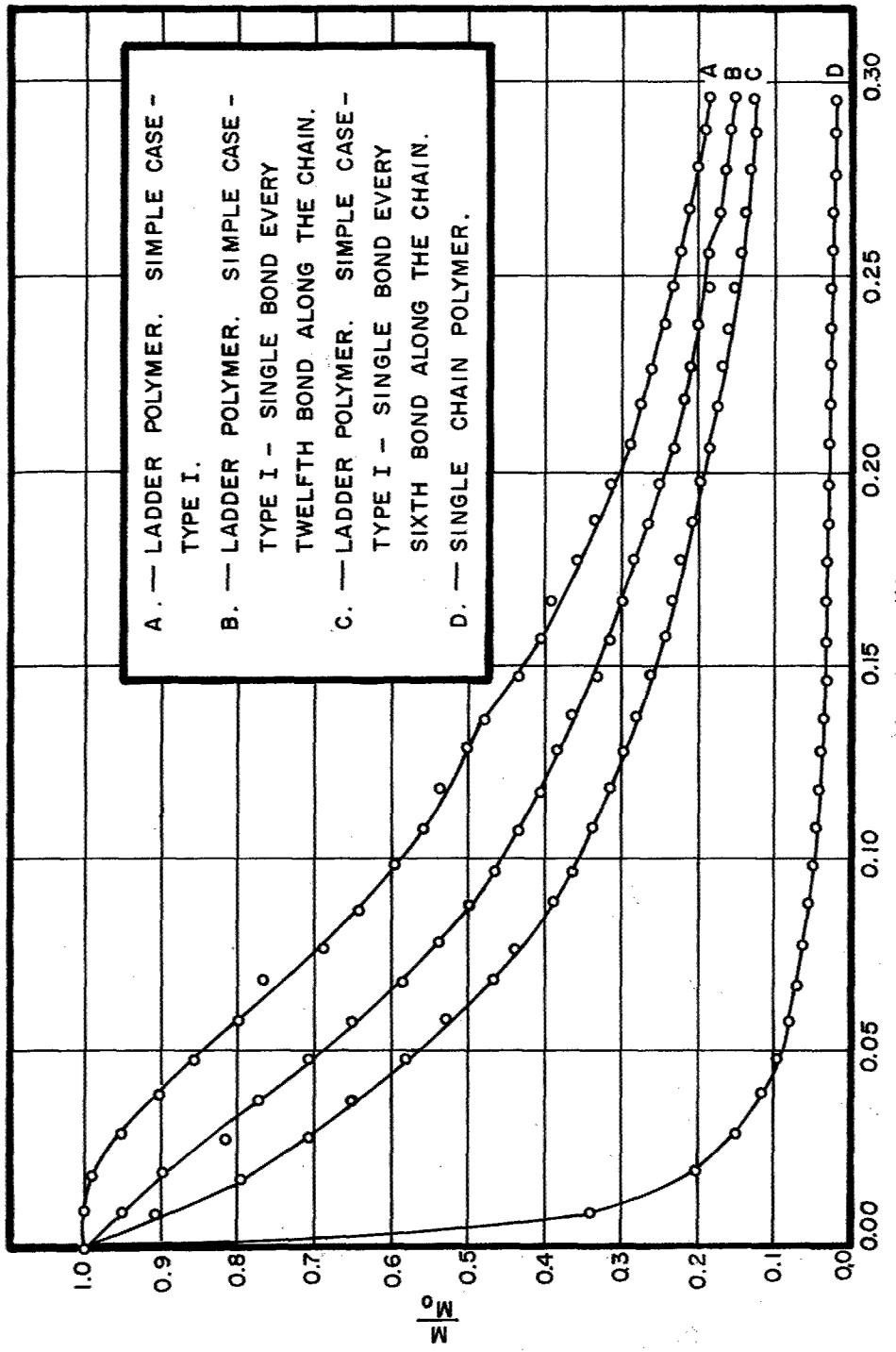

Figure 5. Plot of the Ratio of Molecular Weight to Initial Molecular Weight Versus Time for Different Polymers Undergoing Random Thermal Degradation

A. Ladder Polymer. Simple Case - Type I
B. Ladder Polymer. Simple Case - Type I - Single bond every twelfth bond along the chain
C. Ladder Polymer. Simple Case - Type I - Single bond every sixth bond along the chain
D. Single Chain Polymer

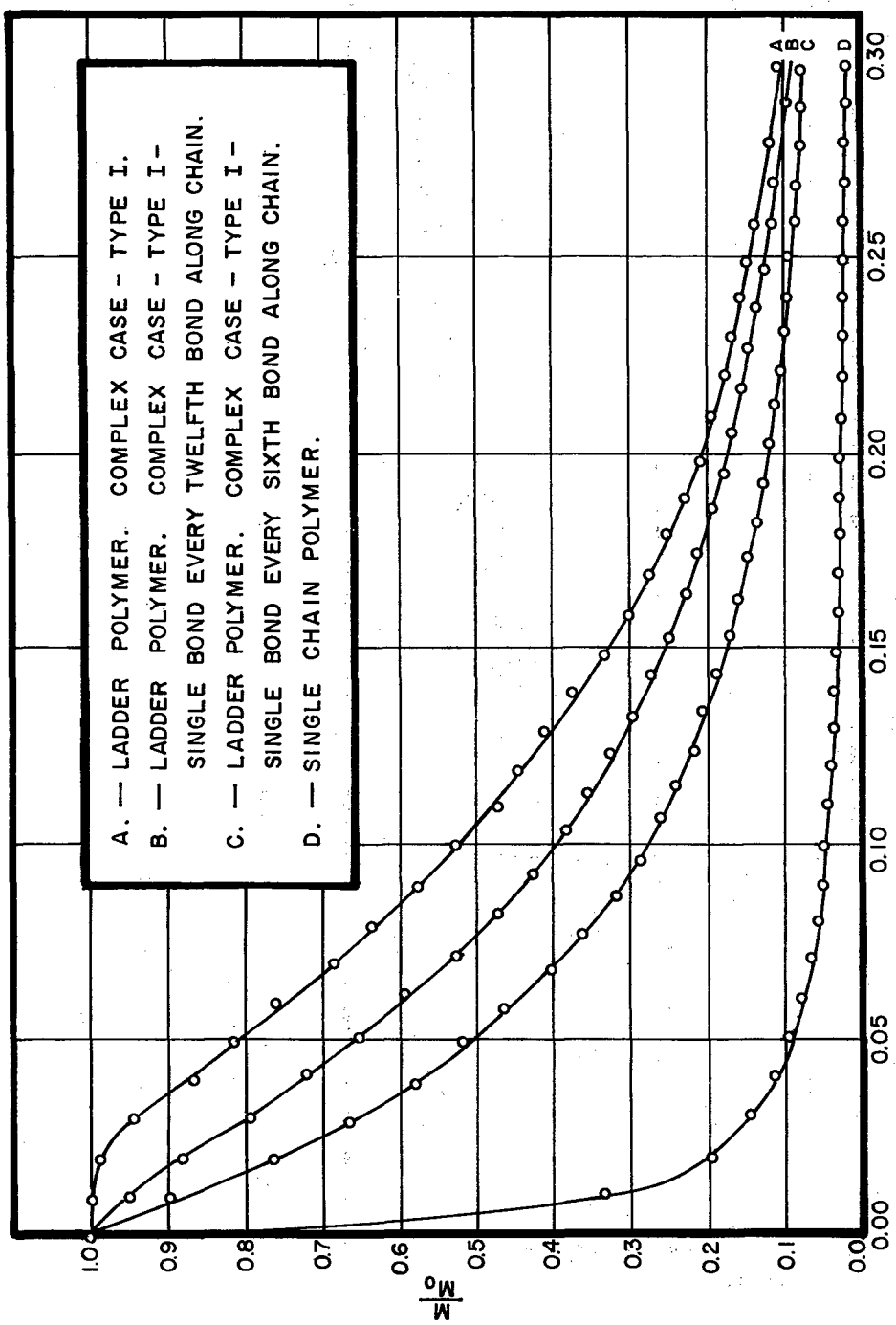

Figure 6. Plot of the Ratio of Molecular Weight to Initial Molecular Weight Versus Time for Different Polymers Undergoing Random Thermal Degradation

A. Ladder Polymer. Complex Case - Type I
B. Ladder Polymer. Complex Case - Type I - Single bond every twelfth bond along chain
C. Ladder Polymer. Complex Case - Type I - Single bond every sixth bond along chain
D. Single Chain Polymer

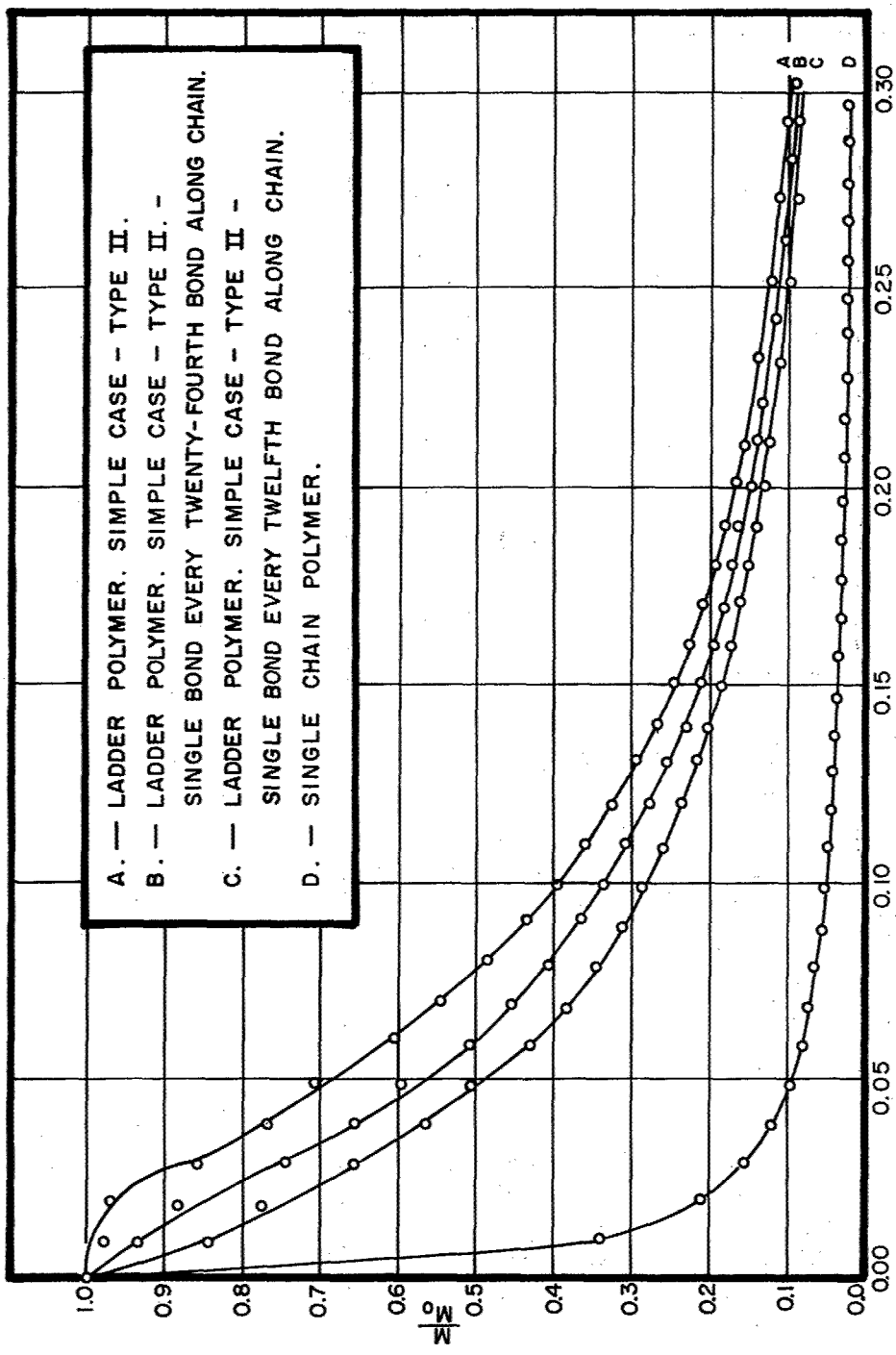

Figure 7. Plot of the Ratio of Molecular Weight to Initial Molecular Weight Versus Time for Different Polymers Undergoing Random Thermal Degradation

A. Ladder Polymer. Simple Case - Type II
B. Ladder Polymer. Simple Case - Type II - Single bond every twenty-fourth bond along chain
C. Ladder Polymer. Simple Case - Type II - Single bond every twelfth bond along chain
D. Single Chain Polymer

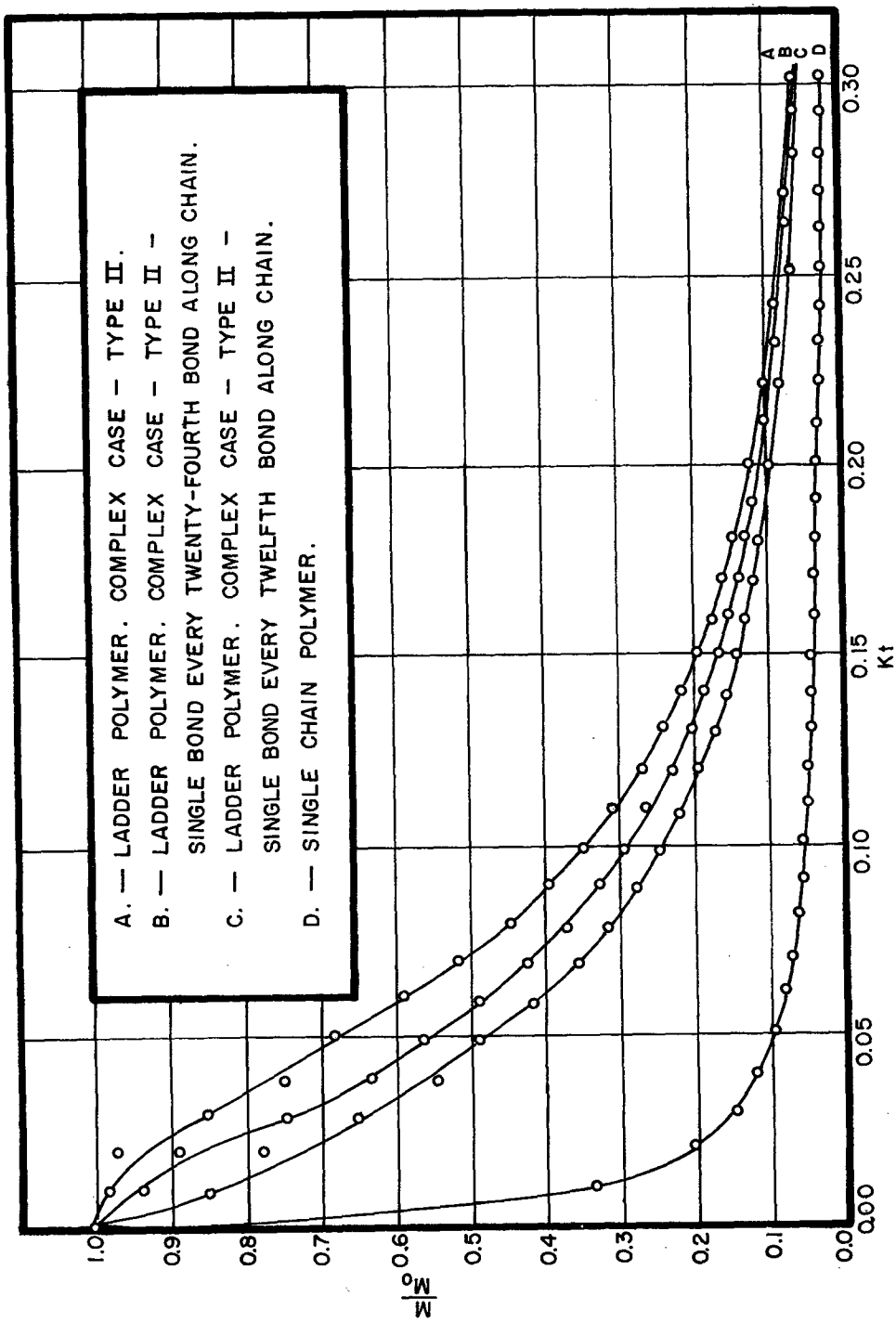

Figure 8. Plot of the Ratio of Molecular Weight to Initial Molecular Weight Versus Time for Different Polymers Undergoing Random Thermal Degradation

A. Ladder Polymer. Complex Case - Type II
B. Ladder Polymer. Complex Case - Type II - Single bond every twenty-fourth bond along chain
C. Ladder Polymer. Complex Case - Type II - Single bond every twelfth bond along chain
D. Single Chain Polymer

APPENDIX I
COMPUTER PROGRAM
SIMPLE CASE. TYPE I

```
C TESSLER LADDER POLYMER DEGRADATION
      DIMENSION L(100,200)
      FREQUENCY 7(1,0,2),8(9,1,0),9(0,1,9),4(1,0,1),10(9,1,0),13(0,1,9)
     1,14(9,1,0)
      NBRAK=0
      NDUP=0
      NLNK=0
      DO 25 IX=1,30
      DO 24 I=1,200
      R=RAND1(Y)*19900.
      NR=R
      ML=NR/199 +1
      NB=199*ML - NR
 7    IF(NB-66)8,8,4
    8 IF(L(ML,NB)-1)28,11,28
   28 L(ML,NB)=1
 9    IF(1-L(ML,NB+66))24, 5,24
    4 IF(NB-132)10,10,14
 10   IF(L(ML,NB)-1)17,11,17
 17   L(ML,NB)=1
 13   IF(1-L(ML,NB-66))24,5,24
 14   IF(L(ML,NB)-1)12,11,12
 12   L(ML,NB)=1
      NLNK=NLNK+1
      GO TO 24
    5 NBRAK=NBRAK +1
      GO TO 24
   11 NDUP=NDUP+1
   24 CONTINUE
      BRK=NBRAK
      ANMW=100./(100.+BRK)
      XI=IX
      DUPN=NDUP
      TIME=LOGF(19900./(19900.-200.*XI+DUPN))
      ASMW=100./(100.+200.*XI-DUPN)
      WRITE OUTPUT TAPE 3,30, NBRAK,NDUP,NLNK,ANMW,ASMW,TIME
   30 FORMAT (1X,3I10,3F20.5)
   25 CONTINUE
      CALL EXIT
      END
```

APPENDIX II
COMPUTER PROGRAM
SIMPLE CASE. TYPE II

```
C TESSLER LADDER POLYMER DEGRADATION FUSED 6 MEMBERED RING
*      XEQ
       DIMENSION L(100,200)
       FREQUENCY 7(1,0,2),8(9,1,0),23(1,1,0),40(0,1,9),42(0,1,9)
      1,41(0,1,9),43(0,1,9),4(2,0,1),10(9,1,0),21(1,1,0),47(0,1,9)
      2,49(0,1,9),48(0,1,9),50(0,1,9),14(0,1,9)
       NBRAK=0
       NDUP=0
       NLNK=0
       DO 25 IX=1,30
       DO 24 I=1,200
       R=RAND1(Y)*19600.
       NR=R
       ML=NR/196+1
       NB=196*ML-NR
     7 IF(NB-78)8,8,4
     8 IF(L(ML,NB)-1)28,11,28
    28 L(ML,NB)=1
       NA=NB/2
    23 IF(2*NA-NB)40,41,40
    40 IF(1-L(ML,NB+78))42,5,42
    42 IF(1-L(ML,NB+79))24,5,24
    41 IF(1-L(ML,NB+78))43,5,43
    43 IF(1-L(ML,NB+77))24,5,24
     4 IF(NB-156)10,10,14
    10 IF(L(ML,NB)-1)17,11,17
    17 L(ML,NB)=1
       NC=NB/2
    21 IF(2*NC-NB)47,48,47
    47 IF(1-L(ML,NB-78))49,5,49
    49 IF(1-L(ML,NB-77))24,5,24
    48 IF(1-L(ML,NB-78))50,5,50
    50 IF(1-L(ML,NB-79))24,5,24
    14 IF(1-L(ML,NB))12,11,12
    12 L(ML,NB)=1
       NLNK=NLNK+1
       GO TO 24
     5 NBRAK=NBRAK+1
       GO TO 24
    11 NDUP=NDUP+1
    24 CONTINUE
       BRK=NBRAK
       ANMW=100./(100.+BRK)
       XI=IX
       DUPN=NDUP
       TIME=LOGF(19600./(19600.-200.*XI+DUPN))



       ASMW=100./(100.+200.*XI-DUPN)
       WRITE OUTPUT TAPE 3,30,NBRAK,NDUP,NLNK,ANMW,ASMW,TIME
    30 FORMAT(1X,3I10,3F20.5)
    25 CONTINUE
       CALL EXIT
       END
)1 (X-  -   (G7                                                    070SQU00
*J -9(NZ5GA 7 -2 -E -G  -  3 5-  - 97 95 -- 94 78 -- -5 -5 -7 -- 4E -4 -070SQU01
*U7(P($T    9 -G  5484 -1 -9 -5 -     2(X)  -  9  -                  070SQU02
```

APPENDIX III
COMPUTER PROGRAM
COMPLEX CASE. TYPE I

```
C TESSLER LADDER POLYMER DEGRADATION WHERE BRAK LNKS CAN YIELD BRAK
*      XEQ
       DIMENSION L(100,200)
       FREQUENCY 7(1,0,2),8(9,1,0),9(0,1,9),31(1,1,9),81(0,1,9),84(0,9,1)
      1,93(0,1,9),54(0,1,9),69(9,1,1),42(0,1,9),44(0,9,1),46(0,1,9)
      2,48(0,1,9),4(1,0,1),32(9,1,0),6(0,1,9),97(1,1,9),35(9,1,0)
      3,36(0,9,1),60(0,1,9),62(0,1,9),68(9,1,1),20(0,1,9),21(0,9,1)
      4,91(0,1,9),27(0,1,9),13(9,1,0),190(1,1,9),191(9,1,0),107(9,1,0)
      5,109(9,1,0),                          111(9,1,1),194(9,1,0),118(9,1,0)
      6,120(9,1,0)
       NBRAK=0
       NDUP=0
       NLNK=0
       DO 25 IX=1,30
       DO 24 I=1,200
       R=RAND1(Y)*19900.
       NR=R
       ML=NR/199+1
       NB=199*ML-NR
 7     IF(NB-66)8,8,4
 8     IF(L(ML,NB)-1)28,11,28
 28    L(ML,NB)=1
 9     IF(1-L(ML,NB+66))80,5,80
C OPPOSITE BOND CHECKED
 80    DO 51 IC=1,67
       NW=NB+133-IC
 31    IF(NW-133)5,81,81
 81    IF(1-L(ML,NW))84,51,84
 51    CONTINUE
C ALL CROSSLINKS TO THE LEFT CHECKED
 84    IF(IC-1)85,75,85
 85    IO=IC-1
       DO 52 KA=1,IO
       NX=NB+66-KA
 93    IF(1-L(ML,NX))53,5,53
C ALL OPPOSITE SIDE LINKS CHECKED
 53    NY=NB-KA
 54    IF(1-L(ML,NY))52,5,52
C ALL ADJACENT SIDE LINKS CHECKED
 52    CONTINUE
 75    DO 17 IC=1,67
       NW=NB+132+IC
 69    IF(NW-199)42,42,5
 42    IF(1-L(ML,NW))44,17,44
 17    CONTINUE
C ALL CROSSLINKS TO THE RIGHT CHECKED
```

```
 44    IF(IC-1)45,24,45
 45    IO=IC-1
       DO 19 KA=1,IO
       NX=NB+66+KA
 46    IF(1-L(ML,NX))47,5,47
C ALL OPPOSITE SIDE LINKS CHECKED
 47    NY=NB+KA
 48    IF(1-L(ML,NY))19,5,19
C ALL ADJACENT SIDE LINKS CHECKED
 19    CONTINUE
       GO TO 24
 4     IF(NB-132)32,32,13
 32    IF(L(ML,NB)-1)33,11,33
 33    L(ML,NB)=1
 6     IF(1-L(ML,NB-66))34,5,34
C OPPOSITE BOND CHECKED
 34    DO 90 IC=1,67
       NW=NB+67-IC
 97    IF(NW-133)5,35,35
 35    IF(L(ML,NW)-1)36,90,36
 90    CONTINUE
C ALL CROSSLINKS TO THE LEFT CHECKED
 36    IF(IC-1)37,38,37
 37    IO=IC-1
       DO 39 KA=1,IO
       NX=NB-66-KA
 60    IF(1-L(ML,NX))61,5,61
C ALL OPPOSITE SIDE LINKS CHECKED
 61    NY=NB-KA
 62    IF(1-L(ML,NY))39,5,39
C ALL ADJACENT SIDE LINKS CHECKED
 39    CONTINUE
 38    DO 63 IC=1,67
       NW=NB+66+IC
 68    IF(NW-199)20,20,5
 20    IF(1-L(ML,NW))21,63,21
 63    CONTINUE
C ALL CROSSLINKS TO THE RIGHT CHECKED
 21    IF(IC-1)22,24,22
 22    IO=IC-1
       DO 23 KA=1,IO
       NX=NB-66+KA
 91    IF(1-L(ML,NX))26,5,26
C ALL OPPOSITE SIDE LINKS CHECKED
 26    NY=NB+KA
 27    IF(1-L(ML,NY))23,5,23
```

```
C ALL ADJACENT SIDE LINKS CHECKED
 23   CONTINUE
      GO TO 24
 13   IF(L(ML,NB)-1)29,11,29
 29   L(ML,NB)=1
      NLNK=NLNK+1
      DO 100 IC=1,67
 190  IF(NB-IC-133)104,102,102
 102  IP=NB-IC
 191  IF(L(ML,IP)-1)105,100,105
 100  CONTINUE
C ALL CROSSLINKS TO THE LEFT CHECKED
 105  DO 106 IW=1,IC
      NX=NB-IW-132
 107  IF(L(ML,NX)-1)108,104,104
 108  NY=NB-IW-66
 109  IF(L(ML,NY)-1)106,104,104
 106  CONTINUE
      GO TO 24
C CHECKED ALL SIDELINKS TO THE LEFT
 104  DO 110 IC=1,67
 111  IF(NB+IC-199)112,112,5
 112  IP=NB+IC
 194  IF(L(ML,IP)-1)116,110,116
 110  CONTINUE
C ALL CROSSLINKS TO THE RIGHT CHECKED
 116  DO 117 IW=1,IC
      NX=NB+IW-133
 118  IF(L(ML,NX)-1)119,5,119
 119  NY=NB+IW-67
 120  IF(L(ML,NY)-1)117,5,117
 117  CONTINUE
C CHECKED ALL SIDELINKS TO THE RIGHT
      GO TO 24
  5   NBRAK=NBRAK+1
      GO TO 24
 11   NDUP=NDUP+1
 24   CONTINUE
      BRK=NBRAK
      ANMW=100./(100.+BRK)
      XI=IX
      DUPN=NDUP
      TIME=LOGF(19900./(19900.-200.*XI+DUPN))
      ASMW=100./(100.+200.*XI-DUPN)
      WRITE OUTPUT TAPE 3,30,NBRAK,NDUP,NLNK,ANMW,ASMW,TIME
 30   FORMAT(1X,3I10,3F20.5)




 25   CONTINUE
      CALL EXIT
      END
```

APPENDIX IV
COMPUTER PROGRAM
COMPLEX CASE. TYPE II

```
C8 TYPE II WHERE CROSSLINK BREAK LEADS TO ADDITIONAL SIDE LINK BREAKS
*       XEQ
        DIMENSION L(100,200)
        FREQUENCY 7(1,0,2),8(9,1,0),92(1,1,0),93(0,1,9),95(0,1,9)
       1,94(0,1,9),96(0,1,9),31(1,1,9),81(0,1,9),84(0,9,1),73(0,1,9)
       2,54(0,1,9),69(9,1,1),42(0,1,9),44(0,9,1),46(0,1,9),48(0,1,9)
       3,4(1,0,1),32(9,1,0),100(1,1,0),98(0,1,9),101(0,1,9),99(0,1,9)
       4,102(0,1,9),97(1,1,9),35(9,1,0),36(0,9,1),60(0,1,9),62(0,1,9)
       5,68(9,1,1),20(0,1,9),21(0,9,1),91(0,1,9),27(0,1,9),13(9,1,0)
       6,190(1,1,9),191(9,1,0),107(9,1,0),109(9,1,0)
       7,111(9,1,1),194(9,1,0),118(9,1,0),120(9,1,0)
        NBRAK=0
        NDUP=0
        NLNK=0
        DO 25 IX=1,30
        DO 24 I=1,200
        R=RAND1(Y)*19600.
        NR=R
        ML=NR/196+1
        NB=196*ML-NR
     7  IF(NB-78)8,8,4
     8  IF(L(ML,NB)-1)28,11,28
    28  L(ML,NB)=1
        NA=NB/2
    92  IF(2*NA-NB)93,94,93
    93  IF(1-L(ML,NB+78))95,5,95
    95  IF(1-L(ML,NB+79))80,5,80
    94  IF(1-L(ML,NB+78))96,5,96
    96  IF(1-L(ML,NB+77))80,5,80
C BOTH OPPOSITE BONDS CHECKED
    80  DO 51 IC=1,41
        NW=NB-NB/2+157-IC
    31  IF(NW-157)5,81,81
    81  IF(1-L(ML,NW))84,51,84
    51  CONTINUE
C ALL CROSSLINKS TO THE LEFT CHECKED
    84  IF(IC-1)85,75,85
    85  IO=(IC-1)*2
        DO 52 KA=1,IO
        NX=((NB+1)/2)*2+77-KA
    73  IF(1-L(ML,NX))53,5,53
C ALL OPPOSITE SIDE LINKS CHECKED
    53  NY=NX-78
    54  IF(1-L(ML,NY))52,5,52
C ALL ADJACENT SIDE LINKS CHECKED
    52  CONTINUE
```

```
   75 DO 17 IC=1,41
      NW=NB-NB/2+156+IC
   69 IF(NW-196)42,42,5
   42 IF(1-L(ML,NW))44,17,44
   17 CONTINUE
C ALL CROSSLINKS TO THE RIGHT CHECKED
   44 IF(IC-1)45,24,45
   45 IO=(IC-1)*2
      DO 19 KA=1,IO
      NX=((NB+1)/2)*2+78+IO
   46 IF(1-L(ML,NX))47,5,47
C ALL OPPOSITE SIDE LINKS CHECKED
   47 NY=NX-78
   48 IF(1-L(ML,NY))19,5,19
C ALL ADJACENT SIDE LINKS CHECKED
   19 CONTINUE
      GO TO 24
    4 IF(NB-156)32,32,13
   32 IF(L(ML,NB)-1)33,11,33
   33 L(ML,NB)=1
      NC=NB/2
  100 IF(2*NC-NB)98,99,98
   98 IF(1-L(ML,NB-78))101,5,101
  101 IF(1-L(ML,NB-77))34,5,34
   99 IF(1-L(ML,NB-78))102,5,102
  102 IF(1-L(ML,NB-79))34,5,34
C OPPOSITE BONDS CHECKED
   34 DO 90 IC=1,41
      NW=NB-NB/2+118-IC
   97 IF(NW-157)5,35,35
   35 IF(L(ML,NW)-1)36,90,36
   90 CONTINUE
C ALL CROSSLINKS TO THE LEFT CHECKED
   36 IF(IC-1)37,38,37
   37 IO=(IC-1)*2
      DO 39 KA=1,IO
      NX=((NB+1)/2)*2-79-KA
   60 IF(1-L(ML,NX))61,5,61
C ALL OPPOSITE SIDE LINKS CHECKED
   61 NY=NX+78
   62 IF(1-L(ML,NY))39,5,39
C ALL ADJACENT SIDE LINKS CHECKED
   39 CONTINUE
   38 DO 63 IC=1,41
      NW=NB-NB/2+117+IC
   68 IF(NW-196)20,20,5
```

```
   20 IF(1-L(ML,NW))21,63,21
   63 CONTINUE
C ALL CROSSLINKS TO THE RIGHT CHECKED
   21 IF(IC-1)22,24,22
   22 IO=(IC-1)*2
      DO 23 KA=1,IO
      NX=((NB+1)/2)*2-78+KA
   91 IF(1-L(ML,NX))26,5,26
C ALL OPPOSITE SIDE LINKS CHECKED
   26 NY=NX+78
   27 IF(1-L(ML,NY))23,5,23
C ALL ADJACENT SIDE LINKS CHECKED
   23 CONTINUE
      GO TO 24
   13 IF(L(ML,NB)-1)29,11,29
   29 L(ML,NB)=1
      NLNK=NLNK+1
      DO 200 IC=1,41
  190 IF(NB-IC-157)104,202,202
  202 IP=NB-IC
  191 IF(L(ML,IP)-1)105,200,105
  200 CONTINUE
C ALL CROSSLINKS TO THE LEFT CHECKED
  105 IBA=2*IC
      DO 106 IW=1,IBA
      NX=2*(NB-156)-1-IW
  107 IF(L(ML,NX)-1)108,104,104
  108 NY=NX+78
  109 IF(L(ML,NY)-1)106,104,104
  106 CONTINUE
      GO TO 24
C CHECKED ALL SIDELINKS TO THE LEFT
  104 DO 110 IC=1,41
  111 IF(NB+IC-196)112,112,5
  112 IP=NB+IC
  194 IF(L(ML,IP)-1)116,110,116
  110 CONTINUE
C ALL CROSSLINKS TO THE RIGHT CHECKED
  116 IBA=2*IC
      DO 117 IW=1,IBA
      NX=2*(NB-157)+78+IW
  118 IF(L(ML,NX)-1)119,5,119
  119 NY=NX-78
  120 IF(L(ML,NY)-1)117,5,117
  117 CONTINUE
C CHECKED ALL SIDELINKS TO THE RIGHT
```

```
      GO TO 24
    5 NBRAK=NBRAK+1
      GO TO 24
   11 NDUP=NDUP+1
   24 CONTINUE
      BRK=NBRAK
      ANMW=100./(100.+BRK)
      XI=IX
      DUPN=NDUP
      TIME=LOGF(19600./(19600.-200.*XI+DUPN))
      ASMW=100./(100.+200.*XI-DUPN)
      WRITE OUTPUT TAPE 3,30,NBRAK,NDUP,NLNK,ANMW,ASMW,TIME
   30 FORMAT(1X,3I10,3F20.5)
   25 CONTINUE
      CALL EXIT
      END
)1 (X-  -   (G7                                                          070SQU00
*.1 -9(NZ5GA 7 -2 -E -G  -  3 5-  - 97 95 -- 94 78 -- -5 -5 -7 -- 4F -4 -070SQU01
*U7(P($T    9 -G  5484 -1 -9 -5 -     2(X)  -  9  -                      070SQU02
```

APPENDIX V
COMPUTER PROGRAM
SIMPLE CASE. TYPE I
SINGLE BOND EVERY SIXTH BOND

```
C15 EVERY SIXTH BOND IS SINGLE CHAIN BOND CALCULATE NAMW CHANGE
C CASE I SIMPLE PROBABILITY FOR ALL BONDS BREAKING IS EQUAL
      DIMENSION L(100,200)
      FREQUENCY 7(1,0,2),8(9,1,0),9(0,1,9),4(1,0,1),10(9,1,0),13(0,1,9)
     1,14(9,1,0)
      NBRAK=0
      NDUP=0
      NLNK=0
      DO 810 MA=1,100
      DO 820 IB=6,66,6
  820 L(MA,IB)=1
  810 CONTINUE
      DO 25 IX=1,30
      DO 24 I=1,200
      R=RAND1(Y)*19900.
      NR=R
      ML=NR/199 +1
      NB=199*ML - NR
    7 IF(NB-66)8,8,4
    8 IF(L(ML,NB)-1)28,11,28
   28 L(ML,NB)=1
    9 IF(1-L(ML,NB+66))24, 5,24
    4 IF(NB-132)10,10,14
   10 IF(L(ML,NB)-1)17,11,17
   17 L(ML,NB)=1
   13 IF(1-L(ML,NB-66))24,5,24
   14 IF(L(ML,NB)-1)12,11,12
   12 L(ML,NB)=1
      NLNK=NLNK+1
      GO TO 24
    5 NBRAK=NBRAK +1
      GO TO 24
   11 NDUP=NDUP+1
   24 CONTINUE
      BRK=NBRAK
      ANMW=100./(100.+BRK)
      XI=IX
      DUPN=NDUP
      TIME=LOGF(18800./(18800.-200.*XI+DUPN))
      ASMW=100./(100.+200.*XI-DUPN)
      WRITE OUTPUT TAPE 3,30, NBRAK,NDUP,NLNK,ANMW,ASMW,TIME
   30 FORMAT (1X,3I10,3F20.5)
   25 CONTINUE
      CALL EXIT
      END
```

APPENDIX VI
COMPUTER PROGRAM
SIMPLE CASE. TYPE I
SINGLE BOND EVERY TWELFTH BOND

```
C CASE I SIMPLE-PROBABILITY FOR ALL BONDS BREAKING IS EQUAL
C16 EVERY TWELVTH BOND IS SINGLE CHAIN BOND -CALCULATE NAMW CHANGE
      DIMENSION L(100,200)
      FREQUENCY 7(1,0,2),8(9,1,0),9(0,1,9),4(1,0,1),10(9,1,0),13(0,1,9)
     1,14(9,1,0)
      NBRAK=0
      NDUP=0
      NLNK=0
      DO 810 MA=1,100
      DO 820 IB=12,66,12
  820 L(MA,IB)=1
  810 CONTINUE
      DO 25 IX=1,30
      DO 24 I=1,200
      R=RAND1(Y)*19900.
      NR=R
      ML=NR/199 +1
      NB=199*ML - NR
    7 IF(NB-66)8,8,4
    8 IF(L(ML,NB)-1)28,11,28
   28 L(ML,NB)=1
    9 IF(1-L(ML,NB+66))24, 5,24
    4 IF(NB-132)10,10,14
   10 IF(L(ML,NB)-1)17,11,17
   17 L(ML,NB)=1
   13 IF(1-L(ML,NB-66))24,5,24
   14 IF(L(ML,NB)-1)12,11,12
   12 L(ML,NB)=1
      NLNK=NLNK+1
      GO TO 24
    5 NBRAK=NBRAK +1
      GO TO 24
   11 NDUP=NDUP+1
   24 CONTINUE
      BRK=NBRAK
      ANMW=100./(100.+BRK)
      XI=IX
      DUPN=NDUP
      TIME=LOGF(19400./(19400.-200.*XI+DUPN))
      ASMW=100./(100.+200.*XI-DUPN)
      WRITE OUTPUT TAPE 3,30, NBRAK,NDUP,NLNK,ANMW,ASMW,TIME
   30 FORMAT (1X,3I10,3F20.5)
   25 CONTINUE
      CALL EXIT
      END
```

APPENDIX VII
COMPUTER PROGRAM
SIMPLE CASE. TYPE II
SINGLE BOND EVERY TWELFTH BOND

```
C19 CASE II SIMPLE EVERY TWELVTH BOND IS SINGLE CHAIN BOND
C PROBABILITY FOR ALL BONDS BREAKING IS EQUAL-CALCULATE NAMW CHANGE
*      XEQ
       DIMENSION L(100,200)
       FREQUENCY 7(1,0,2),8(9,1,0),23(1,1,0),40(0,1,9),42(0,1,9)
      1,41(0,1,9),43(0,1,9),4(2,0,1),10(9,1,0),21(1,1,0),47(0,1,9)
      2,49(0,1,9),48(0,1,9),50(0,1,9),14(0,1,9)
       NBRAK=0
       NDUP=0
       NLNK=0
       DO 810 MA=1,100
       DO 820 IB=12,78,12
 820   L(MA,IB)=1
 810   CONTINUE
       DO 25 IX=1,30
       DO 24 I=1,200
       R=RAND1(Y)*19600.
       NR=R
       ML=NR/196+1
       NB=196*ML-NR
     7 IF(NB-78)8,8,4
     8 IF(L(ML,NB)-1)28,11,28
    28 L(ML,NB)=1
       NA=NB/2
    23 IF(2*NA-NB)40,41,40
    40 IF(1-L(ML,NB+78))42,5,42
    42 IF(1-L(ML,NB+79))24,5,24
    41 IF(1-L(ML,NB+78))43,5,43
    43 IF(1-L(ML,NB+77))24,5,24
     4 IF(NB-156)10,10,14
    10 IF(L(ML,NB)-1)17,11,17
    17 L(ML,NB)=1
       NC=NB/2
    21 IF(2*NC-NB)47,48,47
    47 IF(1-L(ML,NB-78))49,5,49
    49 IF(1-L(ML,NB-77))24,5,24
    48 IF(1-L(ML,NB-78))50,5,50
    50 IF(1-L(ML,NB-79))24,5,24
    14 IF(1-L(ML,NB))12,11,12
    12 L(ML,NB)=1
       NLNK=NLNK+1
       GO TO 24
     5 NBRAK=NBRAK+1
       GO TO 24
    11 NDUP=NDUP+1
    24 CONTINUE
```

```
      BRK=NBRAK
      ANMW=100./(100.+BRK)
      XI=IX
      DUPN=NDUP
      TIME=LOGF(19000./(19000.-200.*XI+DUPN))
      ASMW=100./(100.+200.*XI-DUPN)
      WRITE OUTPUT TAPE 3,30,NBRAK,NDUP,NLNK,ANMW,ASMW,TIME
   30 FORMAT(1X,3I10,3F20.5)
   25 CONTINUE
      CALL EXIT
      END
)1 (X-  -   (G7                                                          070SQU00
*J -9(NZ5GA 7 -2 -E -G  -  3 5-  - 97 95 -- 94 78 -- -5 -5 -7 -- 4E -4 -070SQU01
*U7(P($T    9 -G  5484 -1 -9 -5 -     2(X)  -  9  -                      070SQU02
```

APPENDIX VIII
COMPUTER PROGRAM
SIMPLE CASE. TYPE II
SINGLE BOND EVERY TWENTY-FOURTH BOND

```
C20 CASE II SIMPLE EVERY TWENTY FOURTH BOND IS SINGLE CHAIN BOND
C PROBABILITY FOR ALL BONDS BREAKING IS EQUAL - CALCULATE NAMW CHANGE
*       XEQ
        DIMENSION L(100,200)
        FREQUENCY 7(1,0,2),8(9,1,0),23(1,1,0),40(0,1,9),42(0,1,9)
       1,41(0,1,9),43(0,1,9),4(2,0,1),10(9,1,0),21(1,1,0),47(0,1,9)
       2,49(0,1,9),48(0,1,9),50(0,1,9),14(0,1,9)
        NBRAK=0
        NDUP=0
        NLNK=0
        DO 810 MA=1,100
        DO 820 IB=24,78,24
  820   L(MA,IB)=1
  810   CONTINUE
        DO 25 IX=1,30
        DO 24 I=1,200
        R=RAND1(Y)*19600.
        NR=R
        ML=NR/196+1
        NB=196*ML-NR
      7 IF(NB-78)8,8,4
      8 IF(L(ML,NB)-1)28,11,28
     28 L(ML,NB)=1
        NA=NB/2
     23 IF(2*NA-NB)40,41,40
     40 IF(1-L(ML,NB+78))42,5,42
     42 IF(1-L(ML,NB+79))24,5,24
     41 IF(1-L(ML,NB+78))43,5,43
     43 IF(1-L(ML,NB+77))24,5,24
      4 IF(NB-156)10,10,14
     10 IF(L(ML,NB)-1)17,11,17
     17 L(ML,NB)=1
        NC=NB/2
     21 IF(2*NC-NB)47,48,47
     47 IF(1-L(ML,NB-78))49,5,49
     49 IF(1-L(ML,NB-77))24,5,24
     48 IF(1-L(ML,NB-78))50,5,50
     50 IF(1-L(ML,NB-79))24,5,24
     14 IF(1-L(ML,NB))12,11,12
     12 L(ML,NB)=1
        NLNK=NLNK+1
        GO TO 24
      5 NBRAK=NBRAK+1
        GO TO 24
     11 NDUP=NDUP+1
     24 CONTINUE
```

```
      BRK=NBRAK
      ANMW=100./(100.+BRK)
      XI=IX
      DUPN=NDUP
      TIME=LOGF(19300./(19300.-200.*XI+DUPN))
      ASMW=100./(100.+200.*XI-DUPN)
      WRITE OUTPUT TAPE 3,30,NBRAK,NDUP,NLNK,ANMW,ASMW,TIME
   30 FORMAT(1X,3I10,3F20.5)
   25 CONTINUE
      CALL EXIT
      END
)1 (X-  -   (G7                                                              070SQU00
*J -9(NZ5GA 7 -2 -E -G  -  3 5-  - 97 95 -- 94 78 -- -5 -5 -7 -- 4E -4 -070SQU01
*U7(P(ST    9 -G  5484 -1 -9 -5 -     2(X)  -  9  -                          070SQU02
```

APPENDIX IX
COMPUTER PROGRAM
COMPLEX CASE. TYPE I
SINGLE BOND EVERY SIXTH BOND

```
C17 CASE I COMPLEX-EVERY SIXTH BOND IS SINGLE CHAIN BOND
C PROBABILITY FOR ALL BONDS BREAKING IS EQUAL - CALCULATE NAMW CHANGE
*       XEQ
        DIMENSION L(100,200)
        FREQUENCY 7(1,0,2),8(9,1,0),9(0,1,9),31(1,1,9),81(0,1,9),84(0,9,1)
       1,93(0,1,9),54(0,1,9),69(9,1,1),42(0,1,9),44(0,9,1),46(0,1,9)
       2,48(0,1,9),4(1,0,1),32(9,1,0),6(0,1,9),97(1,1,9),35(9,1,0)
       3,36(0,9,1),60(0,1,9),62(0,1,9),68(9,1,1),20(0,1,9),21(0,9,1)
       4,91(0,1,9),27(0,1,9),13(9,1,0),190(1,1,9),191(9,1,0),107(9,1,0)
       5,109(9,1,0),                          111(9,1,1),194(9,1,0),118(9,1,0)
       6,120(9,1,0)
        NBRAK=0
        NDUP=0
        NLNK=0
        DO 810 MA=1,100
        DO 820 IB=12,66,12
  820   L(MA,IB)=1
  810   CONTINUE
        DO 25 IX=1,30
        DO 24 I=1,200
        R=RAND1(Y)*19900.
        NR=R
        ML=NR/199+1
        NB=199*ML-NR
    7   IF(NB-66)8,8,4
    8   IF(L(ML,NB)-1)28,11,28
   28   L(ML,NB)=1
    9   IF(1-L(ML,NB+66))80,5,80
C OPPOSITE BOND CHECKED
   80   DO 51 IC=1,67
        NW=NB+133-IC
   31   IF(NW-133)3,81,81
   81   IF(1-L(ML,NW))84,51,84
   51   CONTINUE
C ALL CROSSLINKS TO THE LEFT CHECKED
   84   IF(IC-1)85,75,85
   85   IO=IC-1
        DO 52 KA=1,IO
        NX=NB+66-KA
   93   IF(1-L(ML,NX))53,5,53
C ALL OPPOSITE SIDE LINKS CHECKED
   53   NY=NB-KA
   54   IF(1-L(ML,NY))52,5,52
C ALL ADJACENT SIDE LINKS CHECKED
   52   CONTINUE
   75   DO 17 IC=1,67
```

```
      NW=NB+132+IC
 69   IF(NW-199)42,42,5
 42   IF(1-L(ML,NW))44,17,44
 17   CONTINUE
C ALL CROSSLINKS TO THE RIGHT CHECKED
 44   IF(IC-1)45,24,45
 45   IO=IC-1
      DO 19 KA=1,IO
      NX=NB+66+KA
 46   IF(1-L(ML,NX))47,5,47
C ALL OPPOSITE SIDE LINKS CHECKED
 47   NY=NB+KA
 48   IF(1-L(ML,NY))19,5,19
C ALL ADJACENT SIDE LINKS CHECKED
 19   CONTINUE
      GO TO 24
 4    IF(NB-132)32,32,13
 32   IF(L(ML,NB)-1)33,11,33
 33   L(ML,NB)=1
 6    IF(1-L(ML,NB-66))34,5,34
C OPPOSITE BOND CHECKED
 34   DO 90 IC=1,67
      NW=NB+67-IC
 97   IF(NW-133)5,35,35
 35   IF(L(ML,NW)-1)36,90,36
 90   CONTINUE
C ALL CROSSLINKS TO THE LEFT CHECKED
 36   IF(IC-1)37,38,37
 37   IO=IC-1
      DO 39 KA=1,IO
      NX=NB-66-KA
 60   IF(1-L(ML,NX))61,5,61
C ALL OPPOSITE SIDE LINKS CHECKED
 61   NY=NB-KA
 62   IF(1-L(ML,NY))39,5,39
C ALL ADJACENT SIDE LINKS CHECKED
 39   CONTINUE
 38   DO 63 IC=1,67
      NW=NB+66+IC
 68   IF(NW-199)20,20,5
 20   IF(1-L(ML,NW))21,63,21
 63   CONTINUE
C ALL CROSSLINKS TO THE RIGHT CHECKED
 21   IF(IC-1)22,24,22
 22   IO=IC-1
      DO 23 KA=1,IO
```

```
      NX=NB-66+KA
 91   IF(1-L(ML,NX))26,5,26
C ALL OPPOSITE SIDE LINKS CHECKED
 26   NY=NB+KA
 27   IF(1-L(ML,NY))23,5,23
C ALL ADJACENT SIDE LINKS CHECKED
 23   CONTINUE
      GO TO 24
 13   IF(L(ML,NB)-1)29,11,29
 29   L(ML,NB)=1
      NLNK=NLNK+1
      DO 100 IC=1,67
 190  IF(NB-IC-133)104,102,102
 102  IP=NB-IC
 191  IF(L(ML,IP)-1)105,100,105
 100  CONTINUE
C ALL CROSSLINKS TO THE LEFT CHECKED
 105  DO 106 IW=1,IC
      NX=NB-IW-132
 107  IF(L(ML,NX)-1)108,104,104
 108  NY=NB-IW-66
 109  IF(L(ML,NY)-1)106,104,104
 106  CONTINUE
      GO TO 24
C CHECKED ALL SIDELINKS TO THE LEFT
 104  DO 110 IC=1,67
 111  IF(NB+IC-199)112,112,5
 112  IP=NB+IC
 194  IF(L(ML,IP)-1)116,110,116
 110  CONTINUE
C ALL CROSSLINKS TO THE RIGHT CHECKED
 116  DO 117 IW=1,IC
      NX=NB+IW-133
 118  IF(L(ML,NX)-1)119,5,119
 119  NY=NB+IW-67
 120  IF(L(ML,NY)-1)117,5,117
 117  CONTINUE
C CHECKED ALL SIDELINKS TO THE RIGHT
      GO TO 24
 5    NBRAK=NBRAK+1
      GO TO 24
 11   NDUP=NDUP+1
 24   CONTINUE
      BRK=NBRAK
      ANMW=100./(100.+BRK)
      XI=IX




      DUPN=NDUP
      TIME=LOGF(18800./(18800.-200.*XI+DUPN))
      ASMW=100./(100.+200.*XI-DUPN)
      WRITE OUTPUT TAPE 3,30,NBRAK,NDUP,NLNK,ANMW,ASMW,TIME
 30   FORMAT(1X,3I10,3F20.5)
 25   CONTINUE
      CALL EXIT
      END
```

APPENDIX X
COMPUTER PROGRAM
COMPLEX CASE. TYPE I
SINGLE BOND EVERY TWELFTH BOND

```
C18 CASE I COMPLEX EVERY TWELVTH BOND IS SINGLE CHAIN BOND
C PROBABILITY FOR ALL BONDS BREAKING IS EQUAL - CALCULATE NAMW CHANGE
*      XEQ
       DIMENSION L(100,200)
       FREQUENCY 7(1,0,2),8(9,1,0),9(0,1,9),31(1,1,9),81(0,1,9),84(0,9,1)
      1,93(0,1,9),54(0,1,9),69(9,1,1),42(0,1,9),44(0,9,1),46(0,1,9)
      2,48(0,1,9),4(1,0,1),32(9,1,0),6(0,1,9),97(1,1,9),35(9,1,0)
      3,36(0,9,1),60(0,1,9),62(0,1,9),68(9,1,1),20(0,1,9),21(0,9,1)
      4,91(0,1,9),27(0,1,9),13(9,1,0),190(1,1,9),191(9,1,0),107(9,1,0)
      5,109(9,1,0),                          111(9,1,1),194(9,1,0),118(9,1,0)
      6,120(9,1,0)
       NBRAK=0
       NDUP=0
       NLNK=0
       DO 810 MA=1,100
       DO 820 IB=6,66,6
 820   L(MA,IB)=1
 810   CONTINUE
       DO 25 IX=1,30
       DO 24 I=1,200
       R=RAND1(Y)*19900.
       NR=R
       ML=NR/199+1
       NB=199*ML-NR
 7     IF(NB-66)8,8,4
 8     IF(L(ML,NB)-1)28,11,28
 28    L(ML,NB)=1
 9     IF(1-L(ML,NB+66))80,5,80
C OPPOSITE BOND CHECKED
 80    DO 51 IC=1,67
       NW=NB+133-IC
 31    IF(NW-133)5,81,81
 81    IF(1-L(ML,NW))84,51,84
 51    CONTINUE
C ALL CROSSLINKS TO THE LEFT CHECKED
 84    IF(IC-1)85,75,85
 85    IO=IC-1
       DO 52 KA=1,IO
       NX=NB+66-KA
 93    IF(1-L(ML,NX))53,5,53
C ALL OPPOSITE SIDE LINKS CHECKED
 53    NY=NB-KA
 54    IF(1-L(ML,NY))52,5,52
C ALL ADJACENT SIDE LINKS CHECKED
 52    CONTINUE
 75    DO 17 IC=1,67
```

```
      NW=NB+132+IC
 69   IF(NW-199)42,42,5
 42   IF(1-L(ML,NW))44,17,44
 17   CONTINUE
C ALL CROSSLINKS TO THE RIGHT CHECKED
 44   IF(IC-1)45,24,45
 45   IO=IC-1
      DO 19 KA=1,IO
      NX=NB+66+KA
 46   IF(1-L(ML,NX))47,5,47
C ALL OPPOSITE SIDE LINKS CHECKED
 47   NY=NB+KA
 48   IF(1-L(ML,NY))19,5,19
C ALL ADJACENT SIDE LINKS CHECKED
 19   CONTINUE
      GO TO 24
 4    IF(NB-132)32,32,13
 32   IF(L(ML,NB)-1)33,11,33
 33   L(ML,NB)=1
 6    IF(1-L(ML,NB-66))34,5,34
C OPPOSITE BOND CHECKED
 34   DO 90 IC=1,67
      NW=NB+67-IC
 97   IF(NW-133)5,35,35
 35   IF(L(ML,NW)-1)36,90,36
 90   CONTINUE
C ALL CROSSLINKS TO THE LEFT CHECKED
 36   IF(IC-1)37,38,37
 37   IO=IC-1
      DO 39 KA=1,IO
      NX=NB-66-KA
 60   IF(1-L(ML,NX))61,5,61
C ALL OPPOSITE SIDE LINKS CHECKED
 61   NY=NB-KA
 62   IF(1-L(ML,NY))39,5,39
C ALL ADJACENT SIDE LINKS CHECKED
 39   CONTINUE
 38   DO 63 IC=1,67
      NW=NB+66+IC
 68   IF(NW-199)20,20,5
 20   IF(1-L(ML,NW))21,63,21
 63   CONTINUE
C ALL CROSSLINKS TO THE RIGHT CHECKED
 21   IF(IC-1)22,24,22
 22   IO=IC-1
      DO 23 KA=1,IO
```

```
      NX=NB-66+KA
 91   IF(1-L(ML,NX))26,5,26
C ALL OPPOSITE SIDE LINKS CHECKED
 26   NY=NB+KA
 27   IF(1-L(ML,NY))23,5,23
C ALL ADJACENT SIDE LINKS CHECKED
 23   CONTINUE
      GO TO 24
 13   IF(L(ML,NB)-1)29,11,29
 29   L(ML,NB)=1
      NLNK=NLNK+1
      DO 100 IC=1,67
 190  IF(NB-IC-133)104,102,102
 102  IP=NB-IC
 191  IF(L(ML,IP)-1)105,100,105
 100  CONTINUE
C ALL CROSSLINKS TO THE LEFT CHECKED
 105  DO 106 IW=1,IC
      NX=NB-IW-132
 107  IF(L(ML,NX)-1)108,104,104
 108  NY=NB-IW-66
 109  IF(L(ML,NY)-1)106,104,104
 106  CONTINUE
      GO TO 24
C CHECKED ALL SIDELINKS TO THE LEFT
 104  DO 110 IC=1,67
 111  IF(NB+IC-199)112,112,5
 112  IP=NB+IC
 194  IF(L(ML,IP)-1)116,110,116
 110  CONTINUE
C ALL CROSSLINKS TO THE RIGHT CHECKED
 116  DO 117 IW=1,IC
      NX=NB+IW-133
 118  IF(L(ML,NX)-1)119,5,119
 119  NY=NB+IW-67
 120  IF(L(ML,NY)-1)117,5,117
 117  CONTINUE
C CHECKED ALL SIDELINKS TO THE RIGHT
      GO TO 24
 5    NBRAK=NBRAK+1
      GO TO 24
 11   NDUP=NDUP+1
 24   CONTINUE
      BRK=NBRAK
      ANMW=100./(100.+BRK)
      XI=IX



      DUPN=NDUP
      TIME=LOGF(19400./(19400.-200.*XI+DUPN))
      ASMW=100./(100.+200.*XI-DUPN)
      WRITE OUTPUT TAPE 3,30,NBRAK,NDUP,NLNK,ANMW,ASMW,TIME
 30   FORMAT(1X,3I10,3F20.5)
 25   CONTINUE
      CALL EXIT
      END
```

APPENDIX XI
COMPUTER PROGRAM
COMPLEX CASE. TYPE II
SINGLE BOND EVERY TWELFTH BOND

```
C21 CASE II COMPLEX EVERY TWELVTH BOND IS SINGLE CHAIN BOND
C PROBABILITY FOR ALL BONDS BREAKING IS EQUAL - CALCULATE NAMW CHANGE
*       XEQ
        DIMENSION L(100,200)
        FREQUENCY 7(1,0,2),8(9,1,0),92(1,1,0),93(0,1,9),95(0,1,9)
       1,94(0,1,9),96(0,1,9),31(1,1,9),81(0,1,9),84(0,9,1),73(0,1,9)
       2,54(0,1,9),69(9,1,1),42(0,1,9),44(0,9,1),46(0,1,9),48(0,1,9)
       3,4(1,0,1),32(9,1,0),100(1,1,0),98(0,1,9),101(0,1,9),99(0,1,9)
       4,102(0,1,9),97(1,1,9),35(9,1,0),36(0,9,1),60(0,1,9),62(0,1,9)
       5,68(9,1,1),20(0,1,9),21(0,9,1),91(0,1,9),27(0,1,9),13(9,1,0)
       6,190(1,1,9),191(9,1,0),107(9,1,0),109(9,1,0)
       7,111(9,1,1),194(9,1,0),118(9,1,0),120(9,1,0)
        NBRAK=0
        NDUP=0
        NLNK=0
        DO 810 MA=1,100
        DO 820 IB=12,78,12
  820   L(MA,IB)=1
  810   CONTINUE
        DO 25 IX=1,30
        DO 24 I=1,200
        R=RAND1(Y)*19600.
        NR=R
        ML=NR/196+1
        NB=196*ML-NR
    7   IF(NB-78)8,8,4
    8   IF(L(ML,NB)-1)28,11,28
   28   L(ML,NB)=1
        NA=NB/2
   92   IF(2*NA-NB)93,94,93
   93   IF(1-L(ML,NB+78))95,5,95
   95   IF(1-L(ML,NB+79))80,5,80
   94   IF(1-L(ML,NB+78))96,5,96
   96   IF(1-L(ML,NB+77))80,5,80
C BOTH OPPOSITE BONDS CHECKED
   80   DO 51 IC=1,41
        NW=NB-NB/2+157-IC
   31   IF(NW-157)5,81,81
   81   IF(1-L(ML,NW))84,51,84
   51   CONTINUE
C ALL CROSSLINKS TO THE LEFT CHECKED
   84   IF(IC-1)85,75,85
   85   IO=(IC-1)*2
        DO 52 KA=1,IO
        NX=((NB+1)/2)*2+77-KA
   73   IF(1-L(ML,NX))53,5,53
```

```
C ALL OPPOSITE SIDE LINKS CHECKED
   53 NY=NX-78
   54 IF(1-L(ML,NY))52,5,52
C ALL ADJACENT SIDE LINKS CHECKED
   52 CONTINUE
   75 DO 17 IC=1,41
      NW=NB-NB/2+156+IC
   69 IF(NW-196)42,42,5
   42 IF(1-L(ML,NW))44,17,44
   17 CONTINUE
C ALL CROSSLINKS TO THE RIGHT CHECKED
   44 IF(IC-1)45,24,45
   45 IO=(IC-1)*2
      DO 19 KA=1,IO
      NX=((NB+1)/2)*2+78+IO
   46 IF(1-L(ML,NX))47,5,47
C ALL OPPOSITE SIDE LINKS CHECKED
   47 NY=NX-78
   48 IF(1-L(ML,NY))19,5,19
C ALL ADJACENT SIDE LINKS CHECKED
   19 CONTINUE
      GO TO 24
    4 IF(NB-156)32,32,13
   32 IF(L(ML,NB)-1)33,11,33
   33 L(ML,NB)=1
      NC=NB/2
  100 IF(2*NC-NB)98,99,98
   98 IF(1-L(ML,NB-78))101,5,101
  101 IF(1-L(ML,NB-77))34,5,34
   99 IF(1-L(ML,NB-78))102,5,102
  102 IF(1-L(ML,NB-79))34,5,34
C OPPOSITE BONDS CHECKED
   34 DO 90 IC=1,41
      NW=NB-NB/2+118-IC
   97 IF(NW-157)5,35,35
   35 IF(L(ML,NW)-1)36,90,36
   90 CONTINUE
C ALL CROSSLINKS TO THE LEFT CHECKED
   36 IF(IC-1)37,38,37
   37 IO=(IC-1)*2
      DO 39 KA=1,IO
      NX=((NB+1)/2)*2-79-KA
   60 IF(1-L(ML,NX))61,5,61
C ALL OPPOSITE SIDE LINKS CHECKED
   61 NY=NX+78
   62 IF(1-L(ML,NY))39,5,39
```

```
C ALL ADJACENT SIDE LINKS CHECKED
   39 CONTINUE
   38 DO 63 IC=1,41
      NW=NB-NB/2+117+IC
   68 IF(NW-196)20,20,5
   20 IF(1-L(ML,NW))21,63,21
   63 CONTINUE
C ALL CROSSLINKS TO THE RIGHT CHECKED
   21 IF(IC-1)22,24,22
   22 IO=(IC-1)*2
      DO 23 KA=1,IO
      NX=((NB+1)/2)*2-78+KA
   91 IF(1-L(ML,NX))26,5,26
C ALL OPPOSITE SIDE LINKS CHECKED
   26 NY=NX+78
   27 IF(1-L(ML,NY))23,5,23
C ALL ADJACENT SIDE LINKS CHECKED
   23 CONTINUE
      GO TO 24
   13 IF(L(ML,NB)-1)29,11,29
   29 L(ML,NB)=1
      NLNK=NLNK+1
      DO 200 IC=1,41
  190 IF(NB-IC-157)104,202,202
  202 IP=NB-IC
  191 IF(L(ML,IP)-1)105,200,105
  200 CONTINUE
C ALL CROSSLINKS TO THE LEFT CHECKED
  105 IBA=2*IC
      DO 106 IW=1,IBA
      NX=2*(NB-156)-1-IW
  107 IF(L(ML,NX)-1)108,104,104
  108 NY=NX+78
  109 IF(L(ML,NY)-1)106,104,104
  106 CONTINUE
      GO TO 24
C CHECKED ALL SIDELINKS TO THE LEFT
  104 DO 110 IC=1,41
  111 IF(NB+IC-196)112,112,5
  112 IP=NB+IC
  194 IF(L(ML,IP)-1)116,110,116
  110 CONTINUE
C ALL CROSSLINKS TO THE RIGHT CHECKED
  116 IBA=2*IC
      DO 117 IW=1,IBA
      NX=2*(NB-157)+78+IW
```

```
 118   IF(L(ML,NX)-1)119,5,119
 119   NY=NX-78
 120   IF(L(ML,NY)-1)117,5,117
 117   CONTINUE
C CHECKED ALL SIDELINKS TO THE RIGHT
       GO TO 24
     5 NBRAK=NBRAK+1
       GO TO 24
    11 NDUP=NDUP+1
    24 CONTINUE
       BRK=NBRAK
       ANMW=100./(100.+BRK)
       XI=IX
       DUPN=NDUP
       TIME=LOGF(19000./(19000.-200.*XI+DUPN))
       ASMW=100./(100.+200.*XI-DUPN)
       WRITE OUTPUT TAPE 3,30,NBRAK,NDUP,NLNK,ANMW,ASMW,TIME
    30 FORMAT(1X,3I10,3F20.5)
    25 CONTINUE
       CALL EXIT
       END
)1 (X-  -   (G7                                                                070SQU00
*J -9(NZ5GA 7 -2 -E -G  -  3 5-  - 97 95 -- 94 78 -- -5 -5 -7 -- 4E -4 -070SQU01
*J7(P($T    9 -G  5484 -1 -9 -5 -     2(X)  -  9  -                            070SQU02
```

APPENDIX XII
COMPUTER PROGRAM
COMPLEX CASE. TYPE II
SINGLE BOND EVERY TWENTY-FOURTH BOND

```
C22 CASE II COMPLEX - EVERY TWENTY FOURTH BOND IS SINGLE CHAIN BOND
C PROBABILITY FOR ALL BONDS BREAKING IS EQUAL - CALCULATE NAMW CHANGE
*      XEQ
       DIMENSION L(100,200)
       FREQUENCY 7(1,0,2),8(9,1,0),92(1,1,0),93(0,1,9),95(0,1,9)
      1,94(0,1,9),96(0,1,9),31(1,1,9),81(0,1,9),84(0,9,1),73(0,1,9)
      2,54(0,1,9),69(9,1,1),42(0,1,9),44(0,9,1),46(0,1,9),48(0,1,9)
      3,4(1,0,1),32(9,1,0),100(1,1,0),98(0,1,9),101(0,1,9),99(0,1,9)
      4,102(0,1,9),97(1,1,9),35(9,1,0),36(0,9,1),60(0,1,9),62(0,1,9)
      5,68(9,1,1),20(0,1,9),21(0,9,1),91(0,1,9),27(0,1,9),13(9,1,0)
      6,190(1,1,9),191(9,1,0),107(9,1,0),109(9,1,0)
      7,111(9,1,1),194(9,1,0),118(9,1,0),120(9,1,0)
       NBRAK=0
       NDUP=0
       NLNK=0
       DO 810 MA=1,100
       DO 820 IB=24,78,24
 820   L(MA,IB)=1
 810   CONTINUE
       DO 25 IX=1,30
       DO 24 I=1,200
       R=RAND1(Y)*19600.
       NR=R
       ML=NR/196+1
       NB=196*ML-NR
     7 IF(NB-78)8,8,4
     8 IF(L(ML,NB)-1)28,11,28
    28 L(ML,NB)=1
       NA=NB/2
    92 IF(2*NA-NB)93,94,93
    93 IF(1-L(ML,NB+78))95,5,95
    95 IF(1-L(ML,NB+79))80,5,80
    94 IF(1-L(ML,NB+78))96,5,96
    96 IF(1-L(ML,NB+77))80,5,80
C BOTH OPPOSITE BONDS CHECKED
    80 DO 51 IC=1,41
       NW=NB-NB/2+157-IC
    31 IF(NW-157)5,81,81
    81 IF(1-L(ML,NW))84,51,84
    51 CONTINUE
C ALL CROSSLINKS TO THE LEFT CHECKED
    84 IF(IC-1)85,75,85
    85 IO=(IC-1)*2
       DO 52 KA=1,IO
       NX=((NB+1)/2)*2+77-KA
    73 IF(1-L(ML,NX))53,5,53
```

```
C ALL OPPOSITE SIDE LINKS CHECKED
   53 NY=NX-78
   54 IF(1-L(ML,NY))52,5,52
C ALL ADJACENT SIDE LINKS CHECKED
   52 CONTINUE
   75 DO 17 IC=1,41
      NW=NB-NB/2+156+IC
   69 IF(NW-196)42,42,5
   42 IF(1-L(ML,NW))44,17,44
   17 CONTINUE
C ALL CROSSLINKS TO THE RIGHT CHECKED
   44 IF(IC-1)45,24,45
   45 IO=(IC-1)*2
      DO 19 KA=1,IO
      NX=((NB+1)/2)*2+78+IO
   46 IF(1-L(ML,NX))47,5,47
C ALL OPPOSITE SIDE LINKS CHECKED
   47 NY=NX-78
   48 IF(1-L(ML,NY))19,5,19
C ALL ADJACENT SIDE LINKS CHECKED
   19 CONTINUE
      GO TO 24
    4 IF(NB-156)32,32,13
   32 IF(L(ML,NB)-1)33,11,33
   33 L(ML,NB)=1
      NC=NB/2
  100 IF(2*NC-NB)98,99,98
   98 IF(1-L(ML,NB-78))101,5,101
  101 IF(1-L(ML,NB-77))34,5,34
   99 IF(1-L(ML,NB-78))102,5,102
  102 IF(1-L(ML,NB-79))34,5,34
C OPPOSITE BONDS CHECKED
   34 DO 90 IC=1,41
      NW=NB-NB/2+118-IC
   97 IF(NW-157)5,35,35
   35 IF(L(ML,NW)-1)36,90,36
   90 CONTINUE
C ALL CROSSLINKS TO THE LEFT CHECKED
   36 IF(IC-1)37,38,37
   37 IO=(IC-1)*2
      DO 39 KA=1,IO
      NX=((NB+1)/2)*2-79-KA
   60 IF(1-L(ML,NX))61,5,61
C ALL OPPOSITE SIDE LINKS CHECKED
   61 NY=NX+78
   62 IF(1-L(ML,NY))39,5,39
```

```
C ALL ADJACENT SIDE LINKS CHECKED
   39 CONTINUE
   38 DO 63 IC=1,41
      NW=NB-NB/2+117+IC
   68 IF(NW-196)20,20,5
   20 IF(1-L(ML,NW))21,63,21
   63 CONTINUE
C ALL CROSSLINKS TO THE RIGHT CHECKED
   21 IF(IC-1)22,24,22
   22 IO=(IC-1)*2
      DO 23 KA=1,IO
      NX=((NB+1)/2)*2-78+KA
   91 IF(1-L(ML,NX))26,5,26
C ALL OPPOSITE SIDE LINKS CHECKED
   26 NY=NX+78
   27 IF(1-L(ML,NY))23,5,23
C ALL ADJACENT SIDE LINKS CHECKED
   23 CONTINUE
      GO TO 24
   13 IF(L(ML,NB)-1)29,11,29
   29 L(ML,NB)=1
      NLNK=NLNK+1
      DO 200 IC=1,41
  190 IF(NB-IC-157)104,202,202
  202 IP=NB-IC
  191 IF(L(ML,IP)-1)105,200,105
  200 CONTINUE
C ALL CROSSLINKS TO THE LEFT CHECKED
  105 IBA=2*IC
      DO 106 IW=1,IBA
      NX=2*(NB-156)-1-IW
  107 IF(L(ML,NX)-1)108,104,104
  108 NY=NX+78
  109 IF(L(ML,NY)-1)106,104,104
  106 CONTINUE
      GO TO 24
C CHECKED ALL SIDELINKS TO THE LEFT
  104 DO 110 IC=1,41
  111 IF(NB+IC-196)112,112,5
  112 IP=NB+IC
  194 IF(L(ML,IP)-1)116,110,116
  110 CONTINUE
C ALL CROSSLINKS TO THE RIGHT CHECKED
  116 IBA=2*IC
      DO 117 IW=1,IBA
      NX=2*(NB-157)+78+IW
```

```
 118   IF(L(ML,NX)-1)119,5,119
 119   NY=NX-78
 120   IF(L(ML,NY)-1)117,5,117
 117   CONTINUE
C CHECKED ALL SIDELINKS TO THE RIGHT
       GO TO 24
     5 NBRAK=NBRAK+1
       GO TO 24
    11 NDUP=NDUP+1
    24 CONTINUE
       BRK=NBRAK
       ANMW=100./(100.+BRK)
       XI=IX
       DUPN=NDUP
       TIME=LOGF(19300./(19300.-200.*XI+DUPN))
       ASMW=100./(100.+200.*XI-DUPN)
       WRITE OUTPUT TAPE 3,30,NBRAK,NDUP,NLNK,ANMW,ASMW,TIME
    30 FORMAT(1X,3I10,3F20.5)
    25 CONTINUE
       CALL EXIT
       END
)1 (X-  -   (G7                                                              070SQU00
*J -9(NZ5GA 7 -2 -E -G  -  3 5-  - 97 95 -- 94 78 -- -5 -5 -7 -- 4E -4 -070SQU01
*U7(P($T    9 -G  5484 -1 -9 -5 -     2(X)  -  9  -                          070SQU02
```